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Supramolecular chemistry of amine–phenol adducts; novel three-dimensional framework structures in adducts of bis(2-aminoethyl)amine with 4,4′-sulfonyldiphenol, 1,1,1-tris(4-hydroxyphenyl)-ethane and 3,5-dihydroxybenzoic acid, and in the methanol-solvated adduct of tris(2-aminoethyl)-amine with 4,4′-biphenol

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Bis(2-aminoethyl)amine–4,4′-sulfonyldiphenol (1/3) (1) (orthorhombic *Pccn* with $Z' = 0.5$) is a salt, $[HN(CH_2CH_2NH_3)_2]^{2+}.[O_2S(C_6H_4O)_2]^{2-}.[O_2S(C_6H_4OH)_2]_2$, containing both dianionic and neutral bis-phenol units. The neutral and anionic bis-phenol units are linked by strong $O-H\cdots O^-$ hydrogen bonds to form ladders built from $R_4^4(48)$ rings: each ladder is interwoven with its two nearest neighbours to form a continuous two-dimensional sheet. The amine cations play two roles: they link each ladder to its two next-nearest neighbours by means of $N-H\cdots O$ hydrogen bonds and they also link each sheet to the two neighbouring sheets, again *via* $N-H\cdots O$ hydrogen bonds, thus generating a three-dimensional framework. Bis(2-aminoethyl)amine–1,1,1-tris(4-hydroxyphenyl)ethane–methanol (1/4/1) (2) (triclinic $P\bar{1}$ with $Z' = 0.5$) consists entirely of neutral fragments. The tris-phenol units are linked by $O-H\cdots O$ hydrogen bonds into molecular ladders built from $R_4^4(48)$ rings: these ladders are linked by the amine units, firstly into sheets and thence into a three-dimensional framework. Bis(2-aminoethyl)amine–3,5-dihydroxybenzoic acid (1/2) (3) (monoclinic $P2_1/c$ with $Z' = 1$) is a salt $[HN(CH_2CH_2NH_3)_2]^{2+}.[\{(HO)_2C_6H_3COO\}^-]_2$. The 3,5-dihydroxybenzoate anions are linked by $O-H\cdots O$ hydrogen bonds into interwoven and cross-connected (001) sheets linked by further $O-H\cdots O$ hydrogen bonds into a three-dimensional framework. The (001) sheets are further linked by ladders formed from both cations and anions. Tris(2-aminoethyl)amine–4,4′-biphenol–methanol (1/3/1), (4) (monoclinic $P2_1$), is a salt $[\{(H_2NCH_2CH_2)_2N(CH_2CH_2NH_3)\}^+]_2.[OC_6H_4C_6H_4O]^{2-}.[HOC_6H_4C_6H_4OH]_5.[MeOH]_2$, with $Z' = 1$. The asymmetric unit, containing ten independent molecular components, can be regarded as a supermolecule held together by a total of 13 independent hydrogen bonds, of $O-H\cdots O$, $O-H\cdots N$ and $N-H\cdots O$ types. The supermolecules are linked by $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds into two-dimensional sheets, generated by translation; further $N-H\cdots O$ hydrogen bonds around the 2_1 screw axes link neighbouring sheets together into a three-dimensional framework.

1. Introduction

The simple diamine 1,2-diaminoethane exhibits a very rich diversity of hydrogen-bonding behaviour in its adducts with molecular hydroxy compounds. In the 2:1 adduct with 1,1,1-tris(4-hydroxyphenyl)ethane $[CH_3C(C_6H_4OH)_3]_2$.-

$H_2NCH_2CH_2NH_2$ (Ferguson *et al.*, 1998), as well as in $[\{Mn(CO)_3(\mu_3\text{-}OH)\}_4].H_2NCH_2CH_2NH_2$ (Copp *et al.*, 1992), the diamine acts solely as a bis-acceptor of O—H···N hydrogen bonds; in the 2:1 adduct with phenol $(C_6H_5OH)_2.H_2NCH_2CH_2NH_2$ (Loehlin *et al.*, 1994) and in the methanol-solvated 2:1 adduct with 4,4′-biphenol $(HOC_6H_4\text{-}C_6H_4OH)_2.H_2NCH_2CH_2NH_2.MeOH$ (Ferguson *et al.*, 1998) each nitrogen is both an acceptor and a single donor, while in the 1:1 adduct with 4,4′-biphenol, each N atom of the diamine acts as a single donor and double acceptor of hydrogen bonds in a continuous three-dimensional diamondoid network (Ferguson *et al.*, 1998). Only in the 1:1 adduct with 4,4′-biphenol is the idealized complementarity (Ermer & Eling, 1994) of NH_2 groups (as double donors and single acceptors of hydrogen bonds) and OH groups (as single donors and double acceptors) apparent.

In view of this great variety of behaviour exhibited by the diamine $H_2NCH_2CH_2NH_2$, we have now turned our attention to the tri- and tetra-aza analogues bis(2-aminoethyl)amine, $HN(CH_2CH_2NH_2)_2$, and tris(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$, and their behaviour in forming hydrogen-bonded adducts with bis- and tris-phenols. Here we report the preparation and structures of four representative compounds: three, (1)–(3), are adducts of bis(2-aminoethyl)amine with hydrogen-bond donors of steadily increasing complexity, namely 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$, 1,1,1-tris(4-hydroxyphenyl)ethane and 3,5-dihydroxybenzoic acid; the fourth, (4), is a methanol-solvated adduct of tris(2-aminoethyl)amine with 4,4′-biphenol. The selection of 3,5-dihydroxybenzoic acid as one of the molecular building blocks employed in this study was prompted by a consideration of the behaviour of 1,3,5-benzenetricarboxylic acid, trimesic acid, $C_6H_3(COOH)_3$, TMA. TMA is a versatile building block for crystal engineering purposes (Herbstein & Kapon, 1979; Herbstein *et al.*, 1985, 1987; Melendez *et al.*, 1996; Meehan *et al.*, 1997; Ferguson *et al.*, 1998), and in combination with proton–acceptor building blocks this acid can transfer one, two or three protons per molecule to produce a series of anionic species. However, the very versatility of this acid in anion-formation means that its behaviour is largely unpredictable (Melendez *et al.*, 1996). Seeking a structural analogue of TMA with more predictable behaviour and having hydrogen-bond donor and acceptor sites trigonally arranged around a rigid benzenoid core, we thus turned to 3,5-dihydroxybenzoic acid, $C_6H_3(OH)_2COOH$. We reasoned that with amines, one proton would be transferred from the acid to each primary NH_2 group to provide salts of amine cations and the 3,5-dihydroxybenzoate anion: such salts should provide robust hydrogen-bonded solids since all of the hydrogen bonds of O—H···O and N—H···O types could, in principle, involve at least one ionic component.

2. Experimental

2.1. Synthesis

For each combination of amine and phenol, aliquots of each component were separately dissolved in methanol and these solutions were then mixed to give molar ratios of amine: phenol in the range 1:3–3:1 and the mixtures set aside to crystallize. For each combination, a single product resulted regardless of the initial stoichiometry, bis(2-aminoethyl)-amine–4,4′-sulfonyldiphenol (1/3) (1), bis(2-aminoethyl)-amine–1,1,1-tris(4-hydroxyphenyl)ethane–methanol (1/4/1) (2), bis(2-aminoethyl)amine–3,5-dihydroxybenzoic acid (1/2) (3), and tris(2-aminoethyl)amine–4,4′-biphenol–methanol (1/3/1) (4). Analyses: (1) found C 55.5, H 5.1, N 5.0%; $C_{40}H_{43}N_3O_{12}S_3$ requires C 56.3, H 5.1, N 4.9%; (2) found C 74.4, H 6.4, N 3.1%; $C_{85}H_{89}N_3O_{13}$ requires C 75.0, H 6.6, N 3.1%; (3) found C 52.7, H 6.1, N 10.3%; $C_{18}H_{25}N_3O_8$ requires C 52.6, H 6.1, N 10.2%; (4) found C 69.7, H 7.1, N 7.7%; $C_{43}H_{52}N_4O_7$ requires C 70.1, H 7.1, N 7.6%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Details of data collection, and structure solution and refinement are summarized in Table 1.[1] Compound (1) crystallized in the orthorhombic system and the space group was uniquely assigned as *Pccn* from the systematic absences. The unit-cell volume was consistent with there being four molecules of the amine and 12 of the bis-phenol in the *Pccn* cell; this implied that one bis-phenol molecule was in a general position with a second on a twofold axis, while the tris-amine was also on a twofold axis. As the analysis progressed, a difference map showed that the hydroxyl O atoms of the bis-phenol molecule lying about the twofold axis had been deprotonated. The amine was found to lie disordered about a twofold axis; this disorder was successfully modelled and the atoms were selected so that the asymmetric unit contained one complete molecule with all atoms (N, C and H) having 0.5 occupancy. Difference maps in the relevant planes calculated using the COFOUR option of *NRCVAX* (Gabe *et al.*, 1989) clearly showed that the two terminal N atoms (N1, N7) had three H atom sites associated with them and that the central N atom (N4) had pyramidal geometry (2C + 1H).

Compound (2) is triclinic and the space group $P\bar{1}$ was chosen, and subsequently confirmed by the successful solution and refinement. The unit-cell volume was consistent with the presence of four molecules of the tris-phenol and one each of methanol and the triamine. The triamine was found to be disordered across a centre of inversion such that the central nitrogen atom N4 in one orientation was close to one of the terminal nitrogen atoms, N7, in the other orientation. Difference maps showed clearly that there was no transfer of H atoms from hydroxyl groups to the amine.

Compound (3) crystallized in the monoclinic space group $P2_1/c$, uniquely assigned from the systematic absences. Difference maps showed clearly that the carboxyl H atoms of the two independent acid molecules had been transferred to

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0096). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$2(C_{12}H_{10}O_4S).C_{12}H_8O_4S.C_4H_{15}N_3$	$4(C_{20}H_{18}O_3).C_4H_{13}N_3.CH_4O$	$C_4H_{15}N_3.2(C_7H_5O_4)$	$2(C_6H_{19}N_4).5(C_{12}H_{10}O_2).C_{12}H_8O_2.2(CH_4O)$
Chemical formula weight	853.95	1360.59	411.41	1473.77
Cell setting	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	*Pccn*	$P\bar{1}$	$P2_1/c$	$P2_1$
a (Å)	13.7305 (5)	10.7171 (9)	8.2469 (7)	10.0041 (2)
b (Å)	14.9948 (6)	11.2112 (11)	10.527 (2)	41.5502 (7)
c (Å)	19.4209 (9)	15.5547 (19)	23.052 (3)	10.2715 (1)
α (°)	90	101.069 (9)	90	90
β (°)	90	92.924 (9)	98.144 (9)	112.746 (1)
γ (°)	90	97.291 (9)	90	90
V (Å^3)	3998.5 (3)	1813.9 (3)	1981.0 (5)	3937.52 (11)
Z	4	1	4	2
D_x (Mg m^{-3})	1.419	1.245	1.379	1.243
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	23654
θ range (°)	10.56–21.42	9.27–19.31	9.95–15.06	0.98–28.22
μ (mm^{-1})	0.253	0.083	0.109	0.085
Temperature (K)	294 (1)	294 (1)	294 (1)	293 (1)
Crystal form	Block	Plate	Plate	Block
Crystal size (mm)	0.41 × 0.41 × 0.40	0.42 × 0.36 × 0.26	0.41 × 0.41 × 0.22	0.20 × 0.20 × 0.15
Crystal colour	Yellow	Colourless	Colourless	Colourless
Data collection				
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Siemens-CCD
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	ω scans
Absorption correction	None	None	None	None
$T_{\min}$	1.0000	1.0000	–	–
$T_{\max}$	1.0000	1.0000	–	–
No. of measured reflections	4595	6491	3807	23654
No. of independent reflections	4595	6491	3555	9156
No. of observed reflections	3159	4176	1536	6625
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.000	0.000	0.014	0.0397
$\theta_{\max}$ (°)	27.42	25.10	25.15	28.22
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 17$ $0 \rightarrow k \rightarrow 19$ $0 \rightarrow l \rightarrow 25$	$-12 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 13$ $-18 \rightarrow l \rightarrow 18$	$-9 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 12$ $0 \rightarrow l \rightarrow 27$	$-12 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 54$ $0 \rightarrow l \rightarrow 13$
No. of standard reflections	3	3	3	0
Frequency of standard reflections	Every 240 min	Every 120 min	Every 120 min	–
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0391	0.0534	0.0561	0.0572
$wR(F^2)$	0.1077	0.1638	0.0826	0.1433
S	1.042	1.092	0.831	1.047
No. of reflections used in refinement	4595	6491	3555	9156
No. of parameters used	302	495	269	986
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.6244P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0829P)^2 + 0.3479P,]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.8778P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.007	0.000	0.000
$\Delta\rho_{\max}$ (e Å^{-3})	0.284	0.462	0.282	0.175
$\Delta\rho_{\min}$ (e Å^{-3})	−0.234	−0.363	−0.209	−0.209
Extinction method	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient	0.0020 (3)	0.015 (2)	0.0042 (4)	0.0021 (6)

Table 1 (continued)

	(1)	(2)	(3)	(4)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs				
Data collection	*CAD*-4 (Enraf–Nonius, 1992)	*CAD*-4-*PC* Software (Enraf–Nonius, 1992)	*CAD*-4-*PC* Software (Enraf–Nonius, 1992)	*SMART* (Siemens, 1996)
Cell refinement	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SAINT* (Siemens, 1996)
Data reduction	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*SAINT* (Siemens, 1996)
Structure solution	*SHELXS*97 (Sheldrick, 1997*a*)	*SHELXS*97 (Sheldrick, 1997*a*)	*SHELXS*97 (Sheldrick, 1997*a*)	*SHELXS*97 (Sheldrick, 1997*a*)
Structure refinement	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)
Preparation of material for publication	*NRCVAX*96, *SHELXL97* and *WordPerfect* macro *PREP*8 (Ferguson, 1998)	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998)	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998)	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999)

the two terminal N atoms of the amine, but that there was no transfer of any of the phenolic H atoms.

For (4) the systematic absences permitted a choice of space groups, either $P2_1$, with a Z' (Brock & Dunitz, 1994) value of 2, or $P2_1/m$, with $Z' = 1$ for the formula $C_6H_{18}N_4.(C_{12}H_{10}O_2)_3.CH_4O$: the intensity statistics indicated that the space group was not centrosymmetric, and $P2_1$ was confirmed by successful solution and refinement. Difference maps calculated in the vicinity of each of the independent N and O atoms showed that one of the biphenol units had transferred two protons, one to each of the independent amine units, but that all the other components were neutral and hence that the molecular formula must be written as $(C_6H_{19}N_4)_2.(C_{12}H_{10}O_2)_5.C_{12}H_8O_2.(CH_4O)_2$, with $Z' = 1$. The final refinement with non-merged Friedel pairs (15 756 data with 10 902 observed) gave an indeterminate Flack parameter of 0.1 (11): the data in Tables 1–3 were thus derived from a final refinement with merged Friedel pairs. The results of these two refinements differed only in that the s.u. values from the averaged dataset were occasionally larger than those from the full unmerged data by 0.001 Å.

In the final refinement cycles, H atoms were treated as riding atoms (C—H 0.93 and 0.97, N—H 0.89 and 0.90, O—H 0.82 Å). Table 2 contains details of the hydrogen bonding and Table 3 presents selected molecular dimensions. Figs. 1, 7 and 11 show the molecular aggregates in compounds (1)–(3), Figs. 15 and 16 show the independent components and the connected asymmetric unit, respectively, of (4), and Figs. 2–6, 8–10, 12–14, and 16–19 show aspects of the crystal structures of (1)–(4), respectively. The figures were prepared using *PLATON* (Spek, 1999).

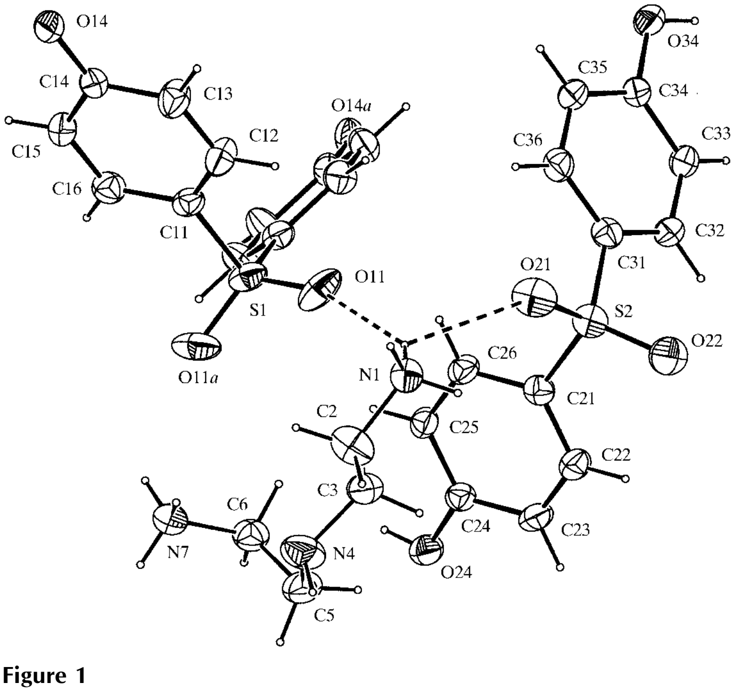

Figure 1
The molecular aggregate in (1), showing the anion $[O_2S(C_6H_4O)_2]^{2-}$ lying across a twofold axis with one orientation of the disordered cation $[HN(CH_2CH_2NH_3)_2]^{2+}$. Displacement ellipsoids are drawn at the 30% probability level.

3. Results and discussion

3.1. Co-crystallization behaviour

The behaviour of bis(2-aminoethyl)amine in (1)–(3) is much more complex than that observed for 1,2-diaminoethane in analogous adducts (Loehlin *et al.*, 1994; Ferguson *et al.*, 1998; Ferguson *et al.*, 1998). In each of (1)–(3) the observed stoichiometries of the crystalline adducts (which are independent, within rather broad limits, of the molar ratio of the reactants in the co-crystallizations) imply that for every two NH_2 groups there are respectively six, 12 and six OH groups present, in addition to any solvent contribution. Similarly in (4) the ratio of NH_2 groups to phenolic OH groups is 1:3. While the stoichiometries deduced initially from elemental analysis were unexpected, and indeed for (1), (2) and (4) seemed implausible, nonetheless all have been confirmed by the X-ray structure analyses described below (§3.2). Clearly, the idealized complementarity of NH_2 and OH groups (Ermer & Eling, 1994) has little influence on these stoichiometries and other factors must underlie any satisfactory explanation of the observed constitutions of (1)–(4).

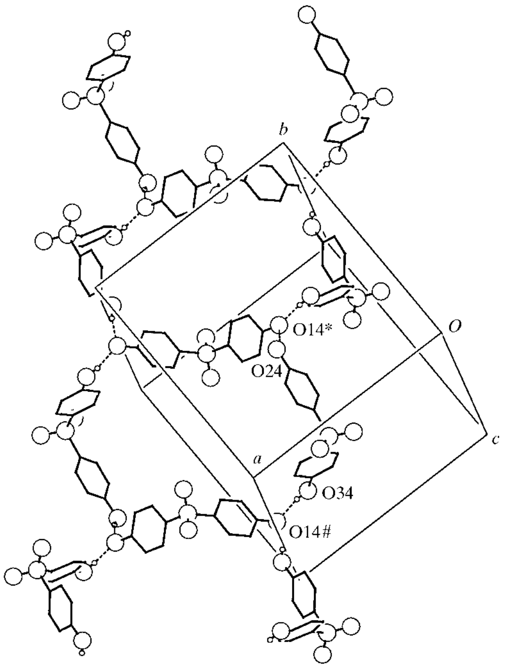

Figure 2
View of part of the crystal structure of (1), showing one of the ladders running parallel to [1$\bar{1}$0] and built from $R_4^4(48)$ rings. H atoms bonded to C are omitted for the sake of clarity. The atoms marked with a star (*) and a hash (#) are at the symmetry positions $(\frac{1}{2}+x, \frac{1}{2}+y, 1-z)$ and $(1+x, y, z)$, respectively.

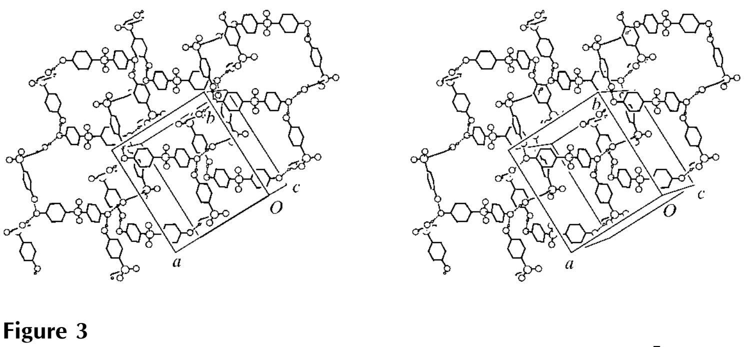

Figure 3
Stereoview of part of the crystal structure of (1), showing a [1$\bar{1}$0] ladder interwoven with its two immediate neighbours to form a sheet parallel to (001). H atoms bonded to C are omitted for the sake of clarity.

3.2. Crystal structures and molecular packing

The crystal structures of (1)–(4) contains, respectively, three, four, three and ten crystallographically independent molecular components. In each compound these molecular components are linked by multiple hydrogen bonds to form a three-dimensional framework. There are two particularly convenient ways to analyse these structures for descriptive purposes. The first is to search for a substructure, often a lower dimensionality than three, built from just one or two of the molecular components: this method has been used successfully in the structure analysis of the compound $[CH_3C(C_6H_4OH)_3]_2.H_2NCH_2CH_2NH_2$ (Ferguson *et al.*, 1998) and in a series of adducts formed by *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazayclotetradecane–2,2′-biphenol with phenols (Gregson *et al.*, 1999). In the present series (1)–(3) all prove to contain amine-free substructures in two, one and three dimensions, respectively.

The second method is to select a 'supermolecule' consisting of at least one asymmetric unit and then to analyse firstly the hydrogen bonding within this aggregate, and secondly the hydrogen-bonding patterns between neighbouring supermolecules. This approach has been adopted here for (4), where the selected supermolecule consists of a single asymmetric unit containing ten independent molecular components. The same approach was originally considered for (1), using as the supermolecule a molecular aggregate containing two asymmetric units (*cf.* Fig. 1): subsequent analysis indicated, however, that the substructure approach provided a more convenient description of the three-dimensional structure of (1).

3.2.1. Bis(2-aminoethyl)amine–4,4′-sulfonyldiphenol (1/3) (1). The asymmetric unit of (1) consists of one bis-phenol molecule in a general position, with another lying across a twofold axis, together with a molecule of the triamine lying in disordered sites across the same twofold axis: the stoichiometric ratio of bis-phenol to triamine molecule is thus 3:1, consistent with the elemental analysis. The triamine molecule actually occupies two sets of sites, each with occupancy 0.5, such that the central nitrogen atom N4 is slightly displaced from the twofold axis. The bis-phenol molecule in the general position is neutral $O_2S(C_6H_4OH)_2$, but that lying across the twofold axis is anionic $[O_2S(C_6H_4O)_2]^{2-}$, having transferred one proton to each of the terminal N atoms of the amine, so that the overall composition of (1) should be described as $[HN(CH_2CH_2NH_3)_2]^{2+}.[O_2S(C_6H_4O)_2]^{2-}.[O_2S(C_6H_4OH)_2]_2$.

There is thus a plethora of potential hydrogen-bond donors and acceptors in the structure. Within the neutral bis-phenol molecule, the hydroxyl oxygen O24 (Fig. 1) acts as a single donor in an O—H···O hydrogen bond and as a double acceptor in N—H···O hydrogen bonds, while the other hydroxyl oxygen O34 acts as a single donor and single acceptor in O—H···O and N—H···O bonds, respectively; the unique anionic oxygen, O14, of the ionized bis-phenol acts as a double acceptor in O—H···O bonds. The sulfone oxygen atoms O11 and O21 each accept one hydrogen bond; although both N1 and N7 act as donors to each of O11 and O21, the half-occupancy of the N1 and N7 sites means an effective average of one N—H···O hydrogen bond for each of N1 and N7. The anion $[O_2S(C_6H_4O)_2]^{2-}$ thus acts as an acceptor of six hard (Braga *et al.*, 1995) hydrogen bonds. Within the triamine dication, one of the terminal nitrogen atoms, N1, acts as a hydrogen-bond donor using all three N—H bonds, to four different O atoms in three different bis-phenol units; the other terminal nitrogen atom, N7, uses only two N—H bonds as donor to three different O atoms in two different bis-phenol units. This difference in behaviour between the two terminal N atoms arises from the slight offset of the central nitrogen N4, and hence of the whole cation, from the twofold axis: if the dication were ordered about the axis, rather than disordered, the N1 and N7 would be symmetry-equivalents. By contrast with the two terminal N atoms, the central nitrogen N4 is unprotonated and acts as neither donor nor acceptor of hydrogen bonds. The positional disorder of the triamine molecule is such that N1 and N7 must be regarded as alternative occupants of what is effectively, although not precisely, a single site. Detailed analysis of the hydrogen bonds involving these two N atoms indicates that it is, for the most part, appropriate to discuss just N1, along with a symmetry-related N1 very close to the refined N7 site. This materially simplifies the analysis and discussion of the supramolecular structure by making full use of the effects of the twofold rotation axis. The O—H···O and N—H···O hydrogen bonds involve all the independent O atoms, except for the sulfone oxygen O22 in the neutral bis-phenol (Table 2). However, as is usually the case in hydrogen-bonded systems involving phenols and primary or secondary amines, there are no intermolecular N—H···N hydrogen bonds; nor are there any O—H···N hydrogen bonds.

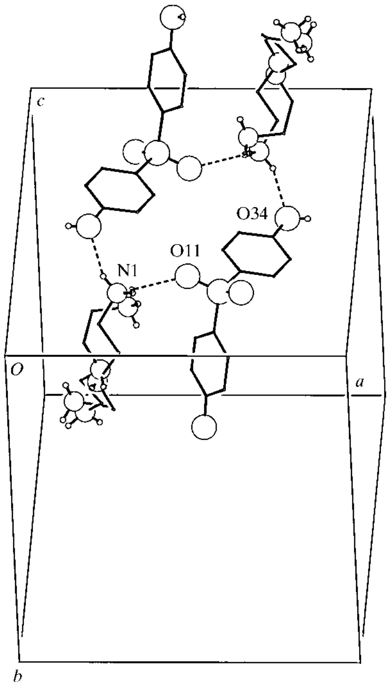

Figure 4
View of part of the crystal structure of (1) showing one of the $R_4^4(20)$ rings which link each $[1\bar{1}0]$ ladder to its next-nearest neighbours within the same (001) sheet. Atoms are depicted as in Fig. 3.

The overall supramolecular architecture in (1) is that of a continuous three-dimensional framework, but it is possible to identify a two-dimensional substructure consisting only of the phenolic components. This substructure takes the form of molecular ladders which are continuously interwoven to form a two-dimensional sheet, rather in the manner of the 2:1 adduct formed between the same bis-phenol with pyrazine (Ferguson *et al.*, 1999). Connections between these nets, provided by the amine dications, then serve to generate the three-dimensional framework.

The molecular ladders run parallel to the $[1\bar{1}0]$ direction (Fig. 2), with the rungs provided by the $[O_2S(C_6H_4O)_2]^{2-}$ anions and the uprights formed by the neutral $O_2S(C_6H_4OH)_2$ molecules. Each neutral bis-phenol acts as hydrogen-bond donor to two different anions, and each anion accepts hydrogen bonds from four different neutral molecules, consistent with the 1:2 ratio of anions to neutral bis-phenols. Oxygen atoms O24 and O34 in the bis-phenol at (x, y, z) act as donors to O14 atoms at $(\frac{1}{2}+x, \frac{1}{2}+y, 1-z)$ and $(1+x, y, z)$, respectively: the anionic O14 at $(\frac{1}{2}+x, \frac{1}{2}+y, 1-z)$ acts as acceptor from the neutral bis-phenols at (x, y, z) and $(-\frac{1}{2}+x, \frac{1}{2}+y, 1-z)$, while the symmetry-related O14 in the same anion lying across the twofold axis $(\frac{3}{4}, \frac{3}{4}, z)$, which is at $(1-x, 1-y, 1-z)$ accepts hydrogen bonds from the two neutral bis-phenols at $(2-x, 1-y, 1-z)$ and $(\frac{3}{2}-x, \frac{3}{2}-y, z)$. Propagation of these interactions generates a sequence of $R_4^4(48)$ rings (Etter, 1990; Bernstein *et al.*, 1995), centred at $(1, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 1, \frac{1}{2})$, $(0, \frac{3}{2}, \frac{1}{2})$ and so on, so forming a ladder parallel to $[1\bar{1}0]$ (Fig. 2).

The formation of this ladder utilizes one bis-phenolate anion and two neutral bis-phenols per unit cell: four such ladders are thus required to generate the entire cell contents in *Pccn*. Two of the ladders lie in

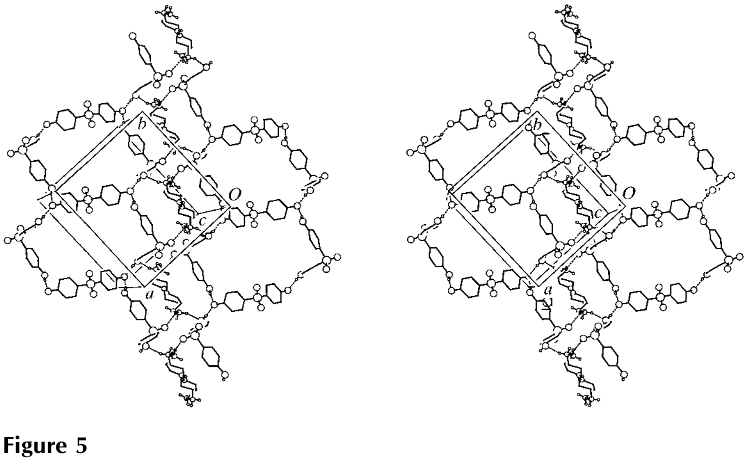

Figure 5
Stereoview of part of the crystal structure of (1) showing the action of the $R_4^4(20)$ rings which link each $[1\bar{1}0]$ ladder to its next-nearest neighbours within the same (001) sheet. Atoms are depicted as in Fig. 3.

the domain $0.28 < z < 0.72$, while the other two lie within $0.78 < z < 1.22$. Within each domain, neighbouring ladders are interwoven, with strands from two neighbouring ladders passing through each of the centrosymmetric $R_4^4(48)$ rings (Fig. 3). The three ladders containing the neutral bis-phenol molecules at $(1+x, y, z)$, (x, y, z) and $(-1+x, y, z)$ are interwoven (Fig. 3): propagation by translation along [100] forms a continuous interwoven sheet parallel to (001), and there are two of these sheets running through each unit cell, in the two domains of z noted above, and related to one another by the action of the c glide planes.

As well as being interwoven with its two immediate neighbours, each ladder within the (001) sheet is also hydrogen-bonded to its next-nearest neighbours *via* the amine dications. In the dication at (x, y, z), N1 acts as a donor to the sulfone oxygen O21 at (x, y, z) and to the hydroxyl oxygen O34 at $(1-x, -y, 1-z)$: these interactions generate a centrosymmetric $R_4^4(20)$ ring (Fig. 4). The ladder containing the neutral bis-phenol at $(1-x, -y, 1-z)$ also contains the neutral bis-phenol at $(-2+x, y, z)$, so generating a direct connection between the bis-phenols at (x, y, z) and $(-2+x, y, z)$: hence these $R_4^4(20)$ motifs serve to connect each ladder to its next-nearest neighbours within the sheet (Fig. 5).

The independent sheets are linked into a continuous three-dimensional network by means of the amine dications. Each amine dication is linked to four different neutral bis-phenol molecules, two of which are in the $0.28 < z < 0.72$ phenol net, while the other two are in the $0.78 < z < 1.22$ phenol net. In the amine dication at (x, y, z) atom N1 acts a donor to sulfone oxygen O21 at (x, y, z) and to hydroxyl oxygen O24 at $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, *via* H1*C* and H1*A*, respectively (Table 2), and atom N7 acts as a donor to O21 at $(\frac{1}{2}-x, \frac{1}{2}-y, z)$ and to O24 at $(-\frac{1}{2}+x, 1-y, \frac{1}{2}-z)$, *via* H7*B* and H7*A*, respectively. Propagation of these interactions leads to a $C_2^2(10)$ chain running parallel to [010] and generated by the 2_1 axis along $(\frac{1}{2}, y, \frac{1}{4})$, and to a $C_2^2(16)$ chain running parallel to [100] and generated by the 2_1 axis along $(x, \frac{1}{2}, \frac{1}{4})$. The intersection of these chains at the cations leads to the generation of a net built from $R_8^8(52)$ rings (Fig. 6). Pendent from each $R_8^8(52)$ ring there are four $-C_6H_4OH$ groups, two on either side of the ring and all roughly normal to its mean plane: these hydroxyl groups on either side form part of the two independent (001) nets. Hence, this motif serves to link together all the (001) nets into a single three-dimensional framework.

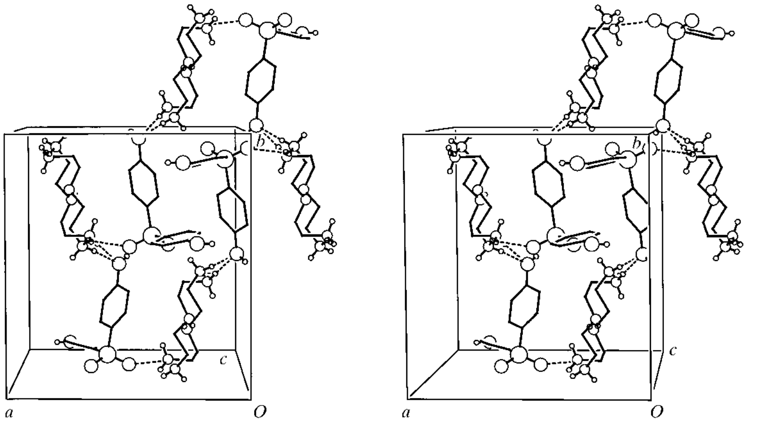

Figure 6
Stereoview of part of the crystal structure of (1) showing one of the $R_8^8(52)$ rings which link the different (001) sheets. Atoms are depicted as in Fig. 3.

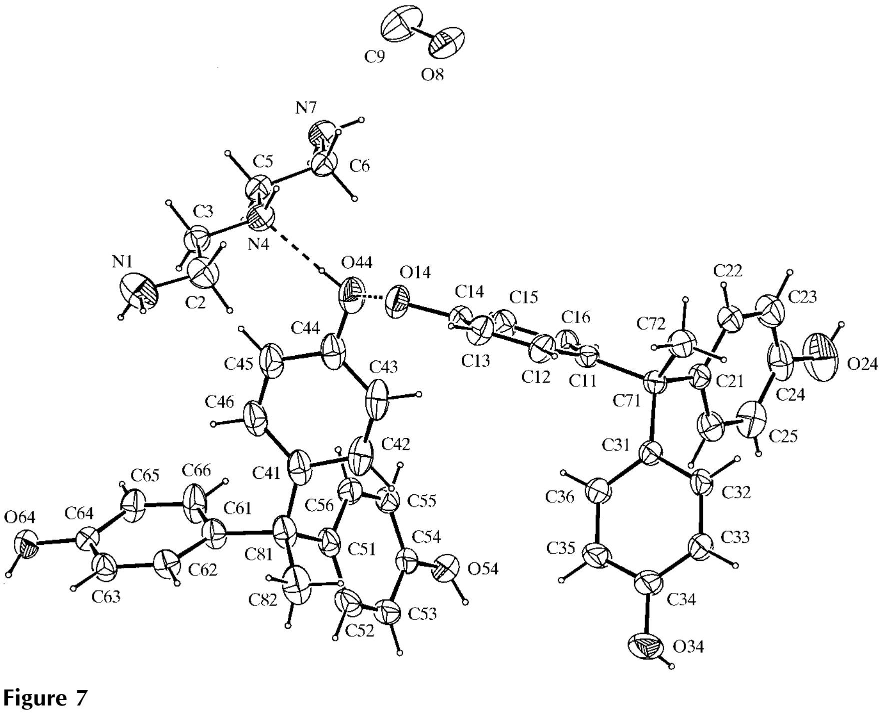

Figure 7
The asymmetric unit in (2), showing one orientation of the disordered amine: the methanol molecule is not placed within the same molecular aggregate as the amine, since otherwise the disordered O8 and N1 occupy very similar sites (see text). Atoms are depicted as in Fig. 1.

3.2.2. Bis(2-aminoethyl)amine–1,1,1-tris(4-hydroxyphenyl)ethane–methanol (1/4/1) (2). The asymmetric unit consists of two molecules of the tris-phenol, both lying in general positions, half a molecule of the triamine and half a molecule of methanol (Fig. 7). The triamine molecules, one per unit cell, are disordered across centres of inversion: the midpoint of the C5—C6 bond is very close to the inversion centre at $(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ so that the N4, C5, C6 and N7 sites in one orientation, at (x, y, z), lie very close to the symmetry-related N7, C6, C5 and N4 sites, respectively, in the other orientation, at $(-1-x, -1-y, 1-z)$. The site of the methanol oxygen O8 at $(1 - x, 1 - y, 1 - z)$ lies very close to the amine N1 site at (x, y, z) and hence it is a reasonable inference that these atoms, O8 and N1, are alternative occupants of this effectively common site (Fig. 8). The reference site actually chosen for the methanol molecule materially eases the illustration of the various components. The presence of methanol at this common site precludes the presence of N1 and hence determines the orientation of the neighbouring amine: regardless of which of N1 and O8 occupies this site, the occupant can and does act as both donor and acceptor of hydrogen bonds. Similarly, the sites occupied by N4 at (x, y, z) and N7 at $(-1 - x, -1 - y, 1 - z)$ are very close, and again these atoms are alternative occupants of an effectively common site.

Subject to this constraint, of the six independent O atoms in the tris-phenol molecules, all but O34 act as hydrogen-bond donors, and all but O24 also act as acceptors. The N1/O8 site acts as both a hydrogen-bond donor and hydrogen-bond acceptor, forming hydrogen bonds with phenolic O atoms in two different molecules. By contrast, N7 and O44 form a closed system, each atom acting as a donor to each other in a four-membered ring. The hydrogen-bonding scheme will be discussed initially in terms of the orientation of the triamine, which excludes the presence of methanol: the alternative orientation, with methanol present, will then be considered.

As with the adduct of 1,1,1-tris(4-hydroxyphenyl)ethane with 1,2-diaminoethane (Ferguson *et al.*, 1998), the supramolecular structure of (2) is best analysed in terms first of the linking of the tris-phenol molecules, and then of the effects of the other structural components. In (2) the tris-phenol molecules are linked into ladders running parallel to the [100]

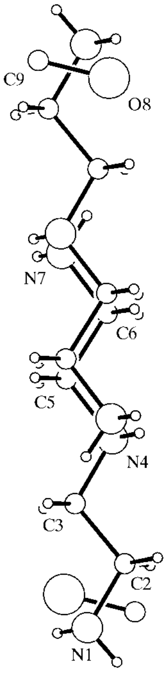

Figure 8
The disordered amine and methanol components in (2), showing the near coincidence of the N4/N7 and N1/O8 sites. Atoms are depicted as spheres with radii in size order H < C < N < O.

Table 2
Hydrogen-bond dimensions (Å, °).

Compound (1)					
O24···O14^{i}	2.496 (2)	H24···O14^{i}	1.67	O24—H24···O14^{i}	164
O34···O14^{ii}	2.533 (2)	H34···O14^{ii}	1.73	O34—H34···O14^{ii}	167
N1···O11	3.037 (4)	H1*C*···O11	2.27	N1—H1*C*···O11	144†
N1···O21	3.056 (4)	H1*C*···O21	2.51	N1—H1*C*···O21	120†
N1···O24^{iii}	2.847 (4)	H1*A*···O24^{iii}	1.96	N1—H1*A*···O24^{iii}	176
N1···O34^{iv}	2.942 (4)	H1*B*···O34^{iv}	2.11	N1—H1*B*···O34^{iv}	156
N7···O24^{v}	2.826 (5)	H7*A*···O24^{v}	1.95	N7—H7*A*···O24^{v}	166
N7···O11^{vi}	2.864 (6)	H7*B*···O11^{vi}	2.37	N7—H7*B*···O11^{vi}	115‡
N7···O21^{vi}	2.799 (5)	H7*B*···O21^{vi}	2.31	N7—H7*B*···O21^{vi}	114‡

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} + y, 1 - z$; (ii) $1 + x, y, z$; (iii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, -y, 1 - z$; (v) $-\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, z$.

Compound (2)					
O14···O44	2.667 (3)	H14···O44	1.87	O14—H14···O44	164
O24···O14^{i}	3.062 (4)	H24···O14^{i}	2.26	O24—H24···O14^{i}	165
O54···O8^{iii}	2.765 (6)	H54···O8^{ii}	2.00	O54—H54···O8^{ii}	156§
O64···O54^{iii}	2.677 (3)	H64···O54^{iii}	1.86	O64—H64···O54^{iii}	173
O44···N4	2.504 (9)	H44···N4	1.69	O44—H44···N4	176¶
O44···N7^{iv}	2.796 (9)	H44···N7^{iv}	2.00	O44—H44···N7^{iv}	164¶
O54···N1^{v}	2.840 (9)	H54···N1^{v}	2.04	O54—H54···N1^{v}	166§
N1···O34^{vi}	3.026 (8)	H1*B*···O34^{vi}	2.15	N1—H1*B*···O34^{vi}	168

Symmetry codes: (i) $-1 + x, y, z$; (ii) $-x, -y, 1 - z$; (iii) $1 + x, y, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $-1 + x, -1 + y, z$; (vi) $1 - x, -y, -z$.

Compound (3)					
O13···O23^{i}	2.668 (3)	H13···O23^{i}	1.99	O13—H13···O23^{i}	140
O15···O12^{ii}	2.703 (4)	H15···O12^{ii}	1.89	O15—H15···O12^{ii}	170
O23···O22^{iii}	2.576 (3)	H23···O22^{iii}	1.79	O23—H23···O22^{iii}	160
O25···O12	2.659 (3)	H25···O12	1.84	O25—H25···O12	172
N1···O21^{iv}	2.936 (4)	H1*A*···O21^{iv}	2.10	N1—H1*A*···O21^{iv}	156
N1···O11^{iv}	2.795 (3)	H1*B*···O11^{iv}	1.95	N1—H1*B*···O11^{iv}	159
N1···O22^{i}	2.790 (4)	H1*C*···O22^{i}	1.95	N1—H1*C*···O22^{i}	158
N7···O13	2.887 (4)	H7*A*···O13	2.06	N7—H7*A*···O13	153
N7···O11^{v}	2.770 (4)	H7*B*···O11^{v}	1.88	N7—H7*B*···O11^{v}	176
N7···O21^{iv}	2.836 (3)	H7*C*···O21^{iv}	2.00	N7—H7*C*···O21^{iv}	157

Symmetry codes: (i) $-x, -y, -z$; (ii) $-1+ x, y, z$; (iii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iv) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (v) $-1 - x, 1 - y, -z$.

Compound (4)					
O2···O3	2.626 (4)	H2···O3	1.82	O2—H2···O3	167
O5···O4	2.620 (4)	H5···O4	1.81	O5—H5···O4	168
O8···O9	2.671 (5)	H8···O9	1.89	O8—H8···O9	158
O11···O10	2.705 (4)	H11···O10	1.90	O11—H11···O10	169
O13···O7	2.758 (5)	H13···O7	2.02	O13—H13···O7	149
O9···O4^{i}	2.502 (4)	H9···O4^{i}	1.71	O9—H9···O4^{i}	162
O10···O3^{ii}	2.496 (5)	H10···O3^{ii}	1.70	O10—H10···O3^{ii}	162
O14···O12^{iii}	2.660 (6)	H14···O12^{iii}	1.86	O14—H14···O12^{iii}	163
O1···N12	2.666 (5)	H1···N12	1.85	O1—H1···N12	172
O6···N21	2.669 (5)	H6···N21	1.86	O6—H6···N21	172
O7···N22^{i}	2.677 (5)	H7···N22^{i}	1.88	O7—H7···N22^{i}	163
O12···N11^{ii}	2.639 (6)	H12···N11^{ii}	1.86	O12—H12···N11^{ii}	157
N11···O1	3.154 (6)	H11*A*···O1	2.28	N11—H11*A*···O1	166
N11···O8^{iv}	3.084 (5)	H11*B*···O8^{iv}	2.21	N11—H11*B*···O8^{iv}	167
N13···O4^{v}	2.780 (5)	H13*A*···O4^{v}	1.93	N13—H13*A*···O4^{v}	158
N13···O1	2.880 (5)	H13*B*···O1	2.08	N13—H13*B*···O1	150
N13···O14	2.746 (7)	H13*C*···O14	1.88	N13—H13*C*···O14	163
N22···O6	3.102 (5)	H22*B*···O6	2.22	N22—H22*B*···O6	171
N23···O3^{vi}	2.788 (5)	H23*A*···O3^{vi}	1.95	N23—H23*A*···O3^{vi}	156
N23···O13	2.805 (6)	H23*B*···O13	2.01	N23—H23*B*···O13	147
N23···O6	2.856 (5)	H23*C*···O6	2.05	N23—H23*C*···O6	150

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, y, 1 + z$; (iii) $-1 + x, y, -1 + z$; (iv) $-x, -\frac{1}{2} + y, 1 - z$; (v) $-1 - x, -\frac{1}{2} + y, 1 - z$; (vi) $-x, \frac{1}{2} + y, 2 - z$. † The angle O11···H1*C*···O21 is 95°, so that the sum of angles around H1*C* is 359°. ‡ The angle O11^{vi}···H7*B*···O21^{vi} is 98°, so that the sum of angles around H1*C* is 327°. § Disordered structure; O8 and N1 are effectively occupants of a common site (see text and Fig. 8). ¶ Disordered structure; N4 and N7 are effectively occupants of a common site (see text and Fig. 8).

direction, and these ladders are linked by the triamine molecules into two-dimensional sheets parallel to $(01\bar{1})$. Each of the two types of tris-phenol molecule (type A containing O14–O34, type B containing O44–O64) forms a $C(12)$ chain parallel to the [100] direction and these two types of chain, both generated by translation, are linked together to form ladders. Atom O24 in the type A tris-phenol at (x, y, z) acts as a donor to O14 at $(-1 + x, y, z)$, while O64 in the type B tris-phenol at (x, y, z) acts as a donor to O54 at $(1 + x, y, z)$. These two antiparallel chains, acting as the uprights of the ladder, are connected by further hydrogen bonds which generate the rungs of the ladder: within the asymmetric unit O14 acts as a donor to O44, and propagation of this interaction by translation completes the ladder (Fig. 9). The reticulations between the rungs of the ladder thus formed are identical and are propagated by translation: these rings are of $R_4^4(38)$ type (Fig. 9). This ladder utilizes one tris-phenol molecule of each type per unit cell and, with the exception of the aryl ring carrying O34, lies almost entirely within the domain $0 < z < 0.5$. There is thus a second such ladder running through each unit cell, related to the first by the action of centres of inversion, and lying largely in the domain $0.5 < z < 1.0$. These ladders are linked by the triamine units to form a three-dimensional framework: for ease of descriptive analysis, this linking can be considered in two stages.

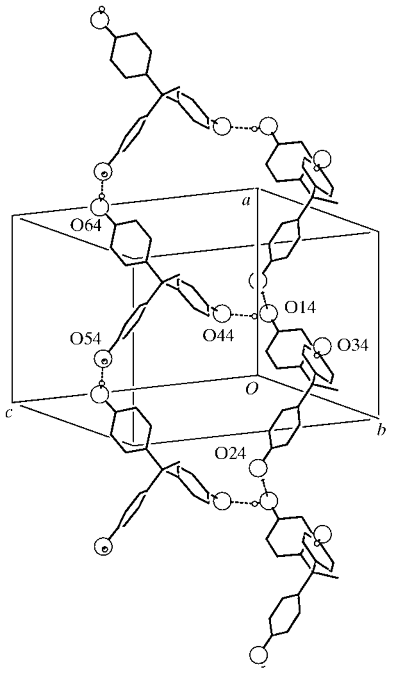

Figure 9
View of part of the crystal structure of (2), showing one of the ladders parallel to [100] built from $R_4^4(38)$ rings. Atoms are depicted as in Fig. 3.

Atom O44 at (x, y, z) acts as donor to N7 at $(-x, -y, 1 - z)$: this N7 is covalently linked to N1 at $(-x, -y, 1 - z)$, which in turn acts as donor to O34 at $(x, 1 + y, 1 + z)$. Atom O14 in the same type A tris-phenol at $(x, 1 + y, 1 + z)$ is donor to O44, also at $(x, 1 + y, 1 + z)$, so producing a chain running parallel to the [011] direction. This chain contains three types of hydrogen bond, one each of N—H···O, O—H···N and O—H···O types. The repeat unit of this chain spans the entire length of a type A tris-phenol, acting as donor and acceptor in O—H···O and N—H···O hydrogen bonds, respectively, the entire length of a triamine molecule acting as donor and acceptor of N—H···O and O—H···N hydrogen bonds, respectively, and one oxygen of a type B tris-phenol acting as donor and acceptor of O—H···N and O—H···O hydrogen bonds, respectively; thus, the graph-set describing the entire chain is $C_3^3(22)$. This chain and the antiparallel chain generated by the action of the inversion centres [*e.g.* at $(0, 0, \frac{1}{2})$] are cross-linked by means of O54 to N1 hydrogen bonds. The tethering of the [100] ladders in this manner generates a thick two-dimensional sheet parallel to $(01\bar{1})$, whose (100) cross-section consists of a series of alternating $R_4^4(40)$ and $R_6^6(52)$ rings, both of which are centrosymmetric, forming a second ladder running parallel to [011] (Fig. 10).

These $(01\bar{1})$ sheets are then further linked to form a three-dimensional framework, by means of the pendent amine dications on each face of each sheet (Fig. 10). Atom O44 in the type B tris-phenol at (x, y, z) acts as donor to N4 at (x, y, z), and N1 in the same dication acts as acceptor from O54 in the type B cation at $(1 + x, 1 + y, z)$, which lies in an adjacent ladder. Thus, a $C_2^2(19)$ chain running parallel to [110] is generated. The interaction of the [100] and [011] ladders and the [110] chains suffice to generate a three-dimensional framework.

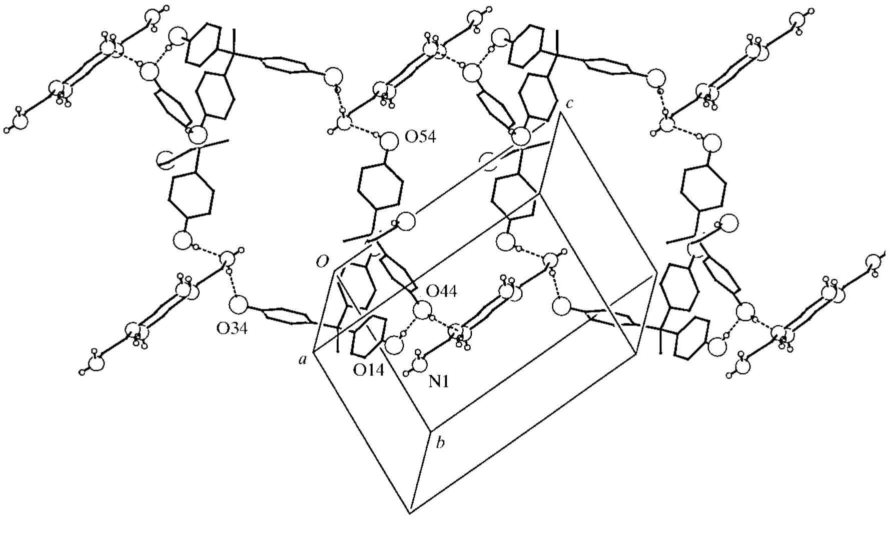

Figure 10
View of part of the crystal structure of (2), showing one of the ladders parallel to [011] built from alternating $R_4^4(40)$ and $R_6^6(52)$ rings. Atoms are depicted as in Fig. 3.

Finally, it is also necessary to consider the hydrogen-bonding scheme when the O8/N1 site is occupied by the methanol O atom: in this case, the alternative $(-1 - x, -1 - y, 1 - z)$ orientation is forced upon the triamine by the presence of the methanol, so that the occupancy of the two N4/N7 sites is reversed. Since the methanol oxygen can act as both donor and acceptor of hydrogen bonds, the larger type of ring within the [011] ladders (Fig. 10) is preserved. Within the triamine at $(-1 - x, -1 - y, 1 - z)$, N4 acts as an acceptor from O44 at $(-x, -y, 1 - z)$, while N1 now acts as a donor to O34 at $(-1 + x, y, 1 + z)$, *i.e.* an O34 atom in the adjacent $(01\bar{1})$ sheet. Hence, with this orientation of the triamine both types of ring (Fig. 10) within the sheets are preserved, and the sheets are linked by hydrogen bonds as well as being interwoven.

3.2.3. Bis(2-aminoethyl)amine–3,5-dihydroxybenzoic acid (1/2) (3). The asymmetric unit in (3) (Fig. 11) consists of one doubly protonated amine and two 3,5-dihydroxybenzoate anions. All the hydrogen atoms in (I) were clearly located from difference maps and all are in ordered sites: the proton transfers from acid to amine are complete, so that (3) must be described as the salt $[HN(CH_2CH_2NH_3)_2]^{2+}.[\{C_6H_3(OH)_2\text{-}COO\}^-]_2$. All six of the terminal N—H bonds of the triamine dication (Fig. 11) are involved in N—H···O hydrogen bonds, and the O—H bonds of the hydroxyl groups are involved in O—H···O hydrogen bonds, so that there are ten independent hydrogen bonds defining the supramolecular structure (Table 2). All the four carboxyl O atoms act as double acceptors of hydrogen bonds: O11 and O21 are both acceptors of two N—H···O hydrogen bonds, O12 is acceptor of two O—H···O hydrogen bonds, while O22 is acceptor in one N—H···O and one O—H···O hydrogen bond. In addition, two of the hydroxyl O atoms, O13 and O23, are acceptors of N—H···O and O—H···O hydrogen bonds, respectively: all the hydrogen bonds, except the last-mentioned, thus involve at least one charged component, while in all of the N—H···O hydrogen bonds to O11, O21 and O22, both components are charged.

Within the asymmetric unit (Fig. 11), atoms N7 and O25 act as donors to O13 and O12, respectively (Table 2).

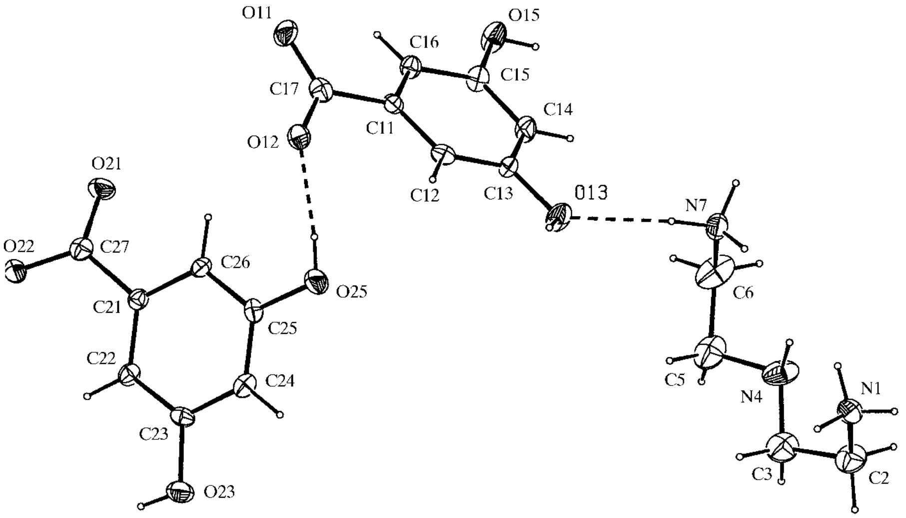

Figure 11
The asymmetric unit of (3). Atoms are depicted as in Fig. 1.

Table 3
Selected geometric parameters (Å, °).

Compound (1)			
N1—C2	1.457 (4)	N4—C5	1.460 (8)
C3—N4	1.460 (8)	C6—N7	1.457 (4)
O14—C14	1.320 (2)		
O24—C24	1.342 (2)	O34—C34	1.350 (2)
N1—C2—C3—N4	−173.8 (6)	C2—C3—N4—C5	169.8 (6)
C3—N4—C5—C6	−84.7 (7)	N4—C5—C6—N7	−51.0 (7)
O11—S1—C11—C12	12.03 (19)	O22—S2—C21—C22	2.48 (17)
O21—S2—C31—C36	−11.15 (17)		
Compound (2)			
N1—C2	1.471 (9)	C3—N4	1.470 (9)
N4—C5	1.477 (9)	C6—N7	1.467 (9)
C14—O14	1.369 (3)	C44—O44	1.377 (4)
C24—O24	1.378 (4)	C54—O54	1.379 (3)
C34—O34	1.378 (3)	C64—O64	1.371 (3)
O8—C9	1.423 (10)		
N1—C2—C3—N4	176.9 (6)	C2—C3—N4—C5	176.1 (6)
C3—N4—C5—C6	177.0 (5)	N4—C5—C6—N7	−179.9 (8)
C12—C11—C71—C72	−49.7 (3)	C42—C41—C81—C82	60.2 (3)
C22—C21—C71—C72	−37.1 (3)	C52—C51—C81—C82	31.7 (3)
C32—C31—C71—C72	−46.2 (3)	C62—C61—C81—C82	18.0 (4)
Compound (3)			
N1—C2	1.491 (4)	C3—N4	1.442 (4)
N4—C5	1.475 (4)	C6—N7	1.477 (4)
O11—C17	1.261 (4)	O21—C27	1.250 (4)
O12—C17	1.257 (4)	O22—C27	1.268 (4)
O13—C13	1.382 (3)	O23—C23	1.374 (4)
O15—C15	1.366 (4)	O25—C25	1.365 (3)
N1—C2—C3—N4	62.5 (4)	C2—C3—N4—C5	−174.1 (3)
C3—N4—C5—C6	178.0 (3)	N4—C5—C6—N7	−65.4 (4)
Interplane angles			
(C11—C16)^(C11,C17,O11,O12)	16.9 (2)		
(C21—C26)^(C21,C27,O21,O22)	27.5 (2)		

Table 3 (continued)

Compound (4)			
N1—C1*A*	1.469 (5)	N2—C1*B*	1.480 (6)
N1—C3*A*	1.467 (5)	N2—C3*B*	1.457 (6)
N1—C5*A*	1.460 (5)	N2—C5*B*	1.455 (5)
N11—C2*A*	1.463 (6)	N21—C2*B*	1.452 (6)
N12—C4*A*	1.468 (6)	N22—C4*B*	1.445 (6)
N13—C6*A*	1.478 (6)	N23—C6*B*	1.505 (6)
O1—C11	1.369 (5)	O2—C21	1.366 (5)
O3—C31	1.357 (4)	O4—C41	1.362 (4)
O5—C51	1.367 (5)	O6—C61	1.367 (5)
O7—C71	1.373 (5)	O8—C81	1.370 (6)
O9—C91	1.360 (5)	O10—C101	1.367 (5)
O11—C111	1.374 (5)	O12—C121	1.371 (5)
O13—C1	1.407 (6)	O14—C2	1.363 (8)
N1—C1*A*—C2*A*—N11	−64.5 (5)	N2—C1*B*—C2*B*—N21	66.4 (5)
N1—C3*A*—C4*A*—N12	−64.8 (5)	N2—C3*B*—C4*B*—N22	70.5 (5)
N1—C5*A*—C6*A*—N13	−60.8 (5)	N2—C5*B*—C6*B*—N23	59.9 (6)
C1*A*—N1—C3*A*—C4*A*	154.1 (4)	C1*B*—N2—C3*B*—C4*B*	79.7 (5)
C3*A*—N1—C5*A*—C6*A*	159.2 (4)	C3*B*—N2—C5*B*—C6*B*	75.6 (5)
C5*A*—N1—C1*A*—C2*A*	159.4 (4)	C5*B*—N2—C1*B*—C2*B*	79.7 (5)
C1*A*—N1—C5*A*—C6*A*	−77.7 (5)	C1*B*—N2—C5*B*—C6*B*	−161.0 (4)
C3*A*—N1—C1*A*—C2*A*	−77.9 (5)	C3*B*—N2—C1*B*—C2*B*	−156.1 (4)
C5*A*—N1—C3*A*—C4*A*	−82.7 (5)	C5*B*—N2—C3*B*—C4*B*	−157.8 (4)
Interplane angles			
(C11—C16)^(C21—C26)	13.2 (1)		
(C31—C36)^(C41—C46)	0.8 (4)		
(C51—C56)^(C61—C66)	7.2 (2)		
(C71—C76)^(C81—C86)	16.6 (2)		
(C91—C96)^(C101—C106)	8.0 (3)		
(C111—C116)^(C121—C126)	9.5 (2)		

The supramolecular structure is most conveniently analysed as a three-dimensional framework built from 3,5-dihydroxybenzoate anions and reinforced by the triamine dications. There are two types of anion in the structure, type *A* containing C1*n* and O1*m* (n = 1–7; m = 1, 2, 3, 5) and type *B* containing C2*n* and O2*m*, and there are four anions of each type per unit cell. Type *B* anions form *C*(7) chains running parallel to the [010] direction, generated by the action of the 2_1 axis along $(\frac{1}{2}, y, \frac{1}{4})$; hydroxyl oxygen O23 at (x, y, z) acts as hydrogen-bond donor to carboxylate oxygen O22 at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, while O23 at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ in turn acts as donor to O22 at $(x, -1 + y, z)$. Formation of this [010] chain utilizes two type *B* molecules per cell, so that there is a second such chain generated by the 2_1 axis along $(\frac{1}{2}, y, \frac{3}{4})$. Type *A* anions form *C*(7) chains running parallel to the [100] direction and generated by translation: hydroxyl oxygen O15 at (x, y, z) acts as hydrogen-bond donor to carboxylate oxygen O12 at $(-1 + x, y, z)$. This [100] chain utilizes just one type *A* anion per unit cell and hence four such chains run through each cell.

The pair of [100] chains related by the 2_1 axis along $(\frac{1}{2}, y, \frac{3}{4})$ are both interwoven with the [010] chains and cross-connected to these chains to form a continuous two-dimensional net parallel to (001). Each [010] chain passes alternately over and under adjacent [100] chains within the net and is connected to them by means of the O25—H···O12 hydrogen bond between the two types of anion within the asymmetric unit (Fig. 12). The cross-connection of these interwoven chains generates a single type of $R_8^6(44)$ ring within the (001) net: the excess of donors over acceptors arises from the two atoms O12 at (x, y, z) and $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ acting as double acceptors. The net built from the [010] chain generated by the 2_1 axis along $(\frac{1}{2}, y, \frac{3}{4})$ and the two [100] chains closest to this axis lies largely in the domain $0 < z < \frac{1}{2}$: a second net involving the [010] chain around $(\frac{1}{2}, y, \frac{3}{4})$ lies largely in the $\frac{1}{2} < z < 1.0$ domain.

The (001) nets are themselves connected into a continuous three-dimensional framework by means of further O—H···O hydrogen bonds (Table 2). The hydroxyl oxygen O13 in the type *A* anion at (x, y, z) acts as hydrogen-bond donor to hydroxyl oxygen O23 in the type *B* anion at $(-x, -y, -z)$. The centre of inversion at the origin thus generates a cyclic centrosymmetric $R_4^4(26)$ motif (Fig. 13), which links the $0 < z < \frac{1}{2}$ net to the $-\frac{1}{2} < z < 0$ net. At the same time, O13 at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ similarly acts as donor to O23 at $(1 + x, -\frac{1}{2} - y, \frac{1}{2} + z)$, so forming another cyclic motif around the centre of inversion at $(1, -\frac{1}{2}, \frac{1}{2})$ and thus linking the $0 < z < \frac{1}{2}$ net to the $\frac{1}{2} < z < 1.0$ net. In this manner all the (001) nets are linked together to form a three-dimensional framework.

The formation of this framework utilizes all four of the independent hydroxyl groups as hydrogen-bond donors, but only two of the carboxylate oxygen atoms, O12 and O22, are

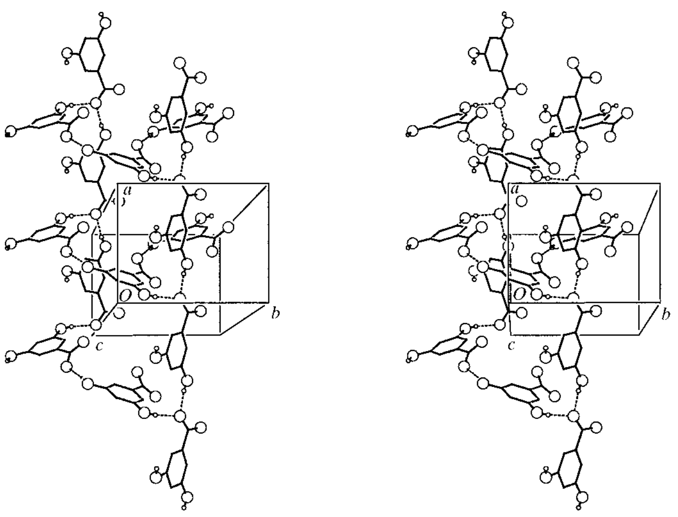

Figure 12
Stereoview of part of the crystal structure of (3) showing the interwoven and interconnected [100] and [010] chains giving rise to an (001) net built from $R_8^6(44)$ rings. Atoms are depicted as in Fig. 3.

involved as acceptors of O—H···O hydrogen bonds. The other two carboxylate O atoms O11 and O21, as well as O11 and O13, act as acceptors of N—H···O hydrogen bonds.

Three of the six terminal N—H bonds in the triamine dication act as donors in N—H···O hydrogen bonds, two to carboxylate oxygen and one to phenolic oxygen, in the formation of a ladder which runs parallel to the $[1\bar{1}0]$ direction, and which serve to link a (001) net to its two immediate neighbours. Nitrogen N7 acts as a donor, *via* H7*A*, to phenolic O13 within the asymmetric unit: N7 at (x, y, z) also acts as a donor, *via* H7*B*, to carboxylate oxygen O11 at $(-1-x, 1-y, -z)$. Atom O13 in the same anion acts as an acceptor from N7, also as $(-1-x, 1-y, -z)$, and this N7 also acts as a donor to carboxylate O11 at (x, y, z). Hence, a cyclic motif, built from four N—H···O hydrogen bonds, is generated around the centre of inversion at $(-\frac{1}{2}, \frac{1}{2}, 0)$ (Fig. 13). The other terminal nitrogen, N1, at (x, y, z) acts as a donor to carboxylate oxygen at $(-x, -y, -z)$: phenolic O25 in the same anion acts as a donor to O12 in the type *A* anion, also at $(-x, -y, -z)$, and O13 in this anion acts as an acceptor from N7, also at $(-x, -y, -z)$. Thus, a second cyclic motif, this time built from four N—H···O and two O—H···O hydrogen bonds, is generated around the centre of inversion at the origin (Fig. 13). Propagation of these two centrosymmetric motifs by the action of centres of inversion generates a ladder parallel to $[1\bar{1}0]$ (Fig. 13): the uprights consist of a repeated three-components sequence, namely the triamine dication, type *B* anion and the carboxylate group of a type *A* anion, while each rung of the ladder is provided by the body of a type *A* anion. There are three types of hydrogen bond within the uprights, one O—H···O and two of the N—H···O type, and this sequence thus has graph-set descriptor $C_3^3(19)$. The entire ladder consists of $R_4^4(18)$ rings around the inversion centres at $[(2n + 1)/2, -(2n + 1)/2, 0]$ (n = 0, 1, 2 *etc.*) alternating with $R_6^6(44)$ rings centred at $(n, -n, 0)$. The centrosymmetric $R_6^6(44)$ rings are themselves divided into one $R_4^4(26)$ sector (Fig. 13) and two $R_3^3(17)$ sectors. Despite its $[1\bar{1}0]$ direction, this ladder serves to link neighbouring (001) nets. The reference (001) nets in the $0 < z < 0.5$ domain contains the carboxylate anions at (x, y, z) and $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$: the triamine at (x, y, z) links this net to that in the $-\frac{1}{2} < z < 0$ domain, while the triamine at $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ links the $0 < z < \frac{1}{2}$ and $\frac{1}{2} < z < 1.0$ nets. Hence, each (001) net is linked by these ladders to its two immediate neighbours.

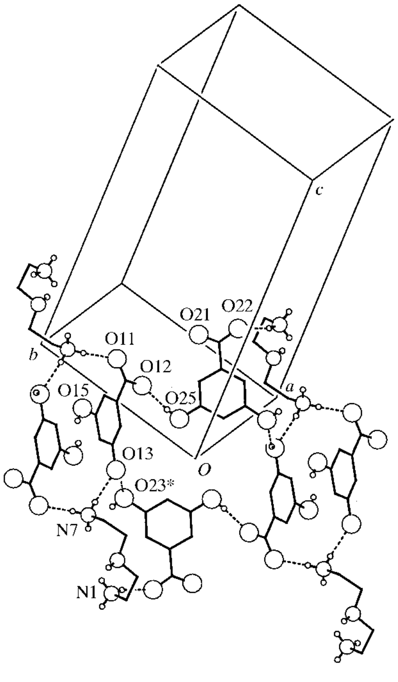

Figure 13
View of part of the crystal structure of (3) showing the ladder parallel to $[1\bar{1}0]$ built from alternating $R_4^4(18)$ and $R_6^6(44)$ rings. H atoms bonded to C are omitted for the sake of clarity. The atom marked with a star (*) is at the symmetry position $(-x, -y, -z)$.

The final hydrogen-bonding motif, utilizing all the remaining donor capacity of the triamine dications and all the remaining acceptor capacity of the carboxylate anions, is a chain-of-rings (Bernstein *et al.*, 1995) running parallel to the [201] direction (Fig. 14) and thus intersecting the stack of (001) nets, and providing further links between them. This [201] chain-of-rings is rather complex (Fig. 14). Atoms N1 and N7 at (x, y, z) both act as donors to O21 at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, generating an $R_2^1(10)$ ring, while N1 at (x, y, z) also acts as a donor to O11 at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$: in combination with the O25—H25···O12 hydrogen bond, the double-donor action of N1 towards O11 and O21 generates an $R_3^3(13)$ ring. These two rings share the N1—H1*A*···O21 hydrogen bond and the overall ring motif, excluding this division, is $R_3^3(19)$. In counting from O13 at (x, y, z) to O13 at $(-1+x, y, z)$, there are two pathways of different length: a $C_2^2(15)$ pathway *via* N1 and avoiding the type *B* anion and a $C_3^3(16)$ pathway *via* the type *B* anion and avoiding N1. Thus, the descriptor for this chain-of-rings can be written in full form as $C_2^2(15)C_3^3(16)$ $[R_2^1(10)]$ $[R_3^3(13)]$, or more concisely as $C_2^2(15)$ $[R_3^3(19)]$.

3.2.4. Tris(2-aminoethyl)amine–4,4′-biphenol–methanol (1/3/1) (4).

Compound (4) crystallizes in the space group

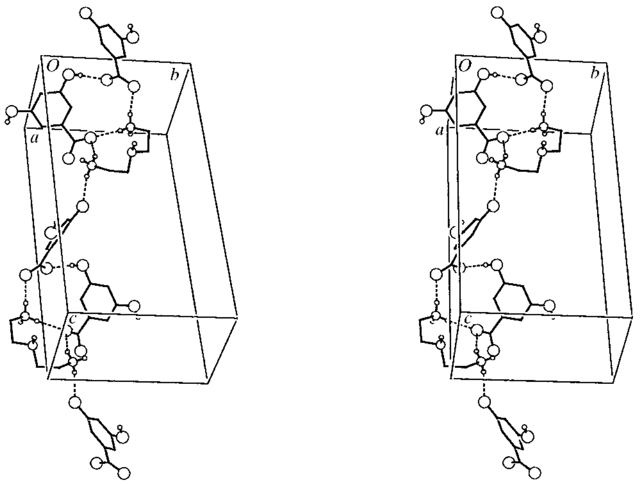

Figure 14
Stereoview of part of the crystal structure of (3) showing the [201] chain-of-rings. Atoms are depicted as in Fig. 3.

$P2_1$ with $Z' = 2$ (Brock & Dunitz, 1994), so that the asymmetric unit contains no fewer than ten molecular components, two molecules each of methanol and the amine, and six molecules of the biphenol. One of the biphenol units is in the form of the dianion $[OC_6H_4C_6H_4O]^{2-}$, having transferred one proton to each of the two amine units: the other five independent biphenol units and both the methanol molecules are neutral (Fig. 15), so that the constitution of (4) is $[\{(H_2NCH_2CH_2)_2N(CH_2CH_2NH_3)\}^+]_2.[OC_6H_4C_6H_4O]^{2-}.[HO-C_6H_4C_6H_4OH]_5.[MeOH]_2$. All the H atoms bonded to oxygen or nitrogen are fully ordered. Each of the amine cations is a donor of six hydrogen bonds and an acceptor of two. Two of the oxygen atoms, O1 and O6, are involved in multiple hydrogen bonds with the tripodal amine units: each of these O atoms is linked to a single cation by means of one O—H···N and two N—H···O hydrogen bonds. Each methanol acts as a donor and an acceptor, respectively, of O—H···O and N—H···O hydrogen bonds.

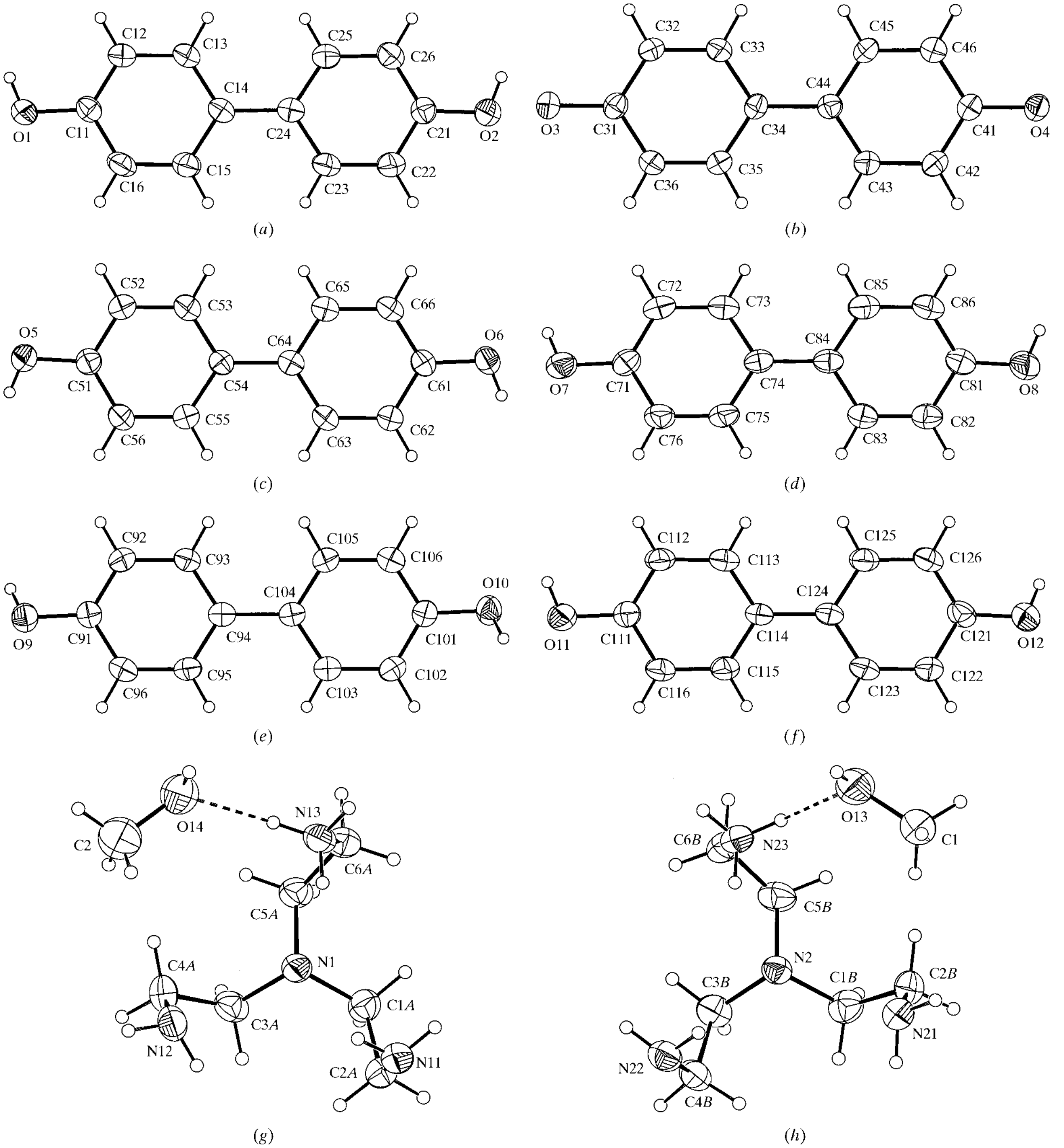

Figure 15
The independent components in (4). Atoms are depicted as in Fig. 1.

Owing to the large number of independent hydrogen bonds within the structure, it is convenient to consider first the hydrogen bonding within the asymmetric unit. While the choice of asymmetric unit in systems such as this is arbitrary, it is convenient and instructive to choose a connected group of molecular components as the asymmetric unit and to treat this as a 'supermolecule', and to consider first the interactions within an individual supermolecule and subsequently those between supermolecules. The simplicity of the space group $P2_1$ means that many of the hydrogen-bonding motifs between supermolecules are generated simply by translations. It should be emphasized that, although the choice of the asymmetric unit is arbitrary, the pattern of hydrogen bonds and the motifs they define is independent of the choice of asymmetric unit. The asymmetric unit selected (Fig. 16) has been chosen to provide a continuous string of singly linked ionic and molecular components, and it takes the form of a folded loop which lies roughly parallel to the long *b* axis of the unit cell. In order to describe and discuss the crystal structure it is convenient first to consider the hydrogen-bonding interactions within the supermolecular aggregate selected as the asymmetric unit, and then to analyse the hydrogen bonds between these supermolecules: this leads to a straightforward description of the three-dimensional hydrogen-bond network.

A minimum of nine hydrogen bonds would be required to connect together the ten components of the asymmetric unit, if each adjacent pair were joined by just one such interaction. In the event, there are 13 hydrogen bonds within the chosen supermolecular aggregate (Table 2). Within the supermolecule there are five O—H···O, six N—H···O and two O—H···N hydrogen bonds. Each amine cation acts as a double donor of hydrogen bonds to, and as a single acceptor from, a single O atom, by the use of all three terminal N atoms, so that the coordination about these two oxygen atoms, O1 and O6, is very approximately tetrahedral, comprising one covalent bond to a C atom and hydrogen bonds involving all three N atoms (Fig. 16, Table 2). In addition, both amine cations form a single N—H···O hydrogen bond to a methanol molecule.

In addition to the hydrogen bonds within the asymmetric unit, there are a further eight distinct interactions between units: five of these are generated by translations in the (010) plane and a further three are generated by the action of the 2_1 screw axes (Table 2). Those generated by translation will be considered first: those involving O12 as a donor and an acceptor serve to link the supermolecules end-to-end into a continuous two-dimensional sheet. Biphenol oxygen O12 at one end of the supermolecule at (x, y, z) (Fig. 16) is a hydrogen-bond donor to N11 at the opposite end of the supermolecule at $(x, y, 1 + z)$. Propagation of this interaction by translation generates a continuous $C_9^9(72)$ chain running in the [001] direction and consisting of parallel supermolecules. The same O12 at (x, y, z) also acts as an acceptor from the methanol oxygen O14 at the far end of the supermolecule at $(1 + x, y, 1 + z)$: propagation of this interaction links the parallel supermolecules into a $C_{10}^{10}(74)$ chain running parallel to [101]. The effectiveness of these two types of hydrogen bond in tying the supermolecules into a two-dimensional sheet depends upon the fact that although O12 is separated from O14 and N11 in the same supermolecule by a very large number of bonds, all three atoms have very similar *y* coordinates and hence can readily form hydrogen bonds by translation in the (010) plane.

The formation of this two-dimensional array is reinforced by three other types of hydrogen bond: O10 at (x, y, z) acts as hydrogen-bond donor to the anionic O3 at $(x, y, 1 + z)$, thus reinforcing the [001] chain formation; and O9 and O7 at (x, y, z) act as donors to, respectively, O4 and N22 at $(1 + x, y, z)$, so forming chains parallel to [100] and effectively cross-bracing the two-dimensional net formed by the intersection of [001] and [101] chains. Hence, these five types of hydrogen bond, generated by translation, together form a very tightly bound two-dimensional array.

The (010) nets thus formed are themselves linked into a continuous three-dimensional network by means of a further series of three hydrogen bonds, all of N—H···O type, generated by the action of the 2_1 screw axes. One of these hydrogen bonds links the initial sheet, generated by translation from the supermolecule at (x, y, z), to the adjacent sheet in the [010] direction and the other two link this initial sheet to its neighbour in the $[0\bar{1}0]$ direction (Table 2). The hydrogen-bonding interactions between neighbouring sheets follow directly from the mutual arrangement of the components within the supermolecule (Fig. 16): there are amine cations, rich in N—H bonds at either end of the supermolecule, centred around $y = 0$ and $y = 0.85$, respectively, while there is a group of O atoms (O2–O5 and O8–O11), all potential hydrogen-bond acceptors, about half-way along the supermolecule with *y* coordinates in the range 0.30–0.55. Hence, a translation of $y/2$, consequent upon the action of the 2_1 axis, brings the terminal NH bonds of one supermolecule into close proximity with the oxygen-rich regions of other symmetry-related supermolecules. The

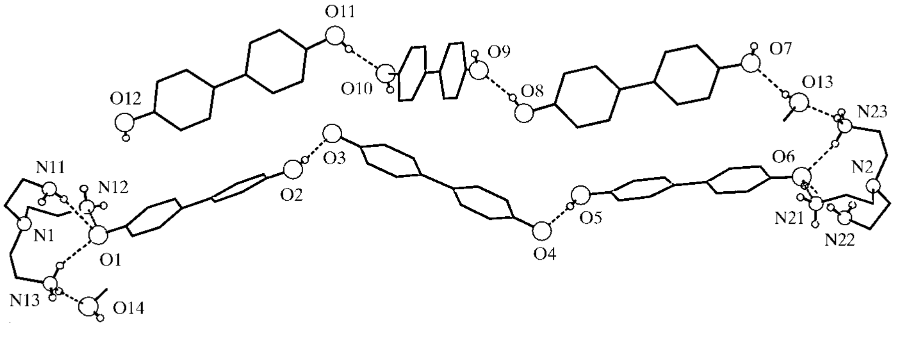

Figure 16
The asymmetric unit of (4), showing the labelling of the O and N atoms. Atoms are depicted as in Fig. 3.

N23 atom at (x, y, z) acts as a donor to O3 at $(-x, \frac{1}{2}+y, 2-z)$, generating a $C_3^3(24)$ spiral chain around the screw axis at $(0, y, 1)$ (Fig. 17). In the second amine cation, centred around $y = 0$, N11 at (x, y, z) acts as a donor to O8 at $(-x, -\frac{1}{2}+y, 1-z)$, generating a $C_7^7(50)$ spiral around the screw axis at $(0, y, \frac{1}{2})$ (Fig. 18) and atom N13 at (x, y, z) acts as a donor to O4 at $(-1-x, -\frac{1}{2}+y, 1-z)$, thus generating a $C_3^3(20)$ spiral around the screw axis at $(-\frac{1}{2}, y, \frac{1}{2})$ (Fig. 19).

3.2.5. General comments on the structures of (1)–(4). The structures described above show that unlike 1,2-diaminoethane, both the amines used in this study are able to effect proton transfer from bis-phenols. Not only are the stoichiometries of (1)–(4) in general unexpected, but the acid–base properties underlying them are also instructive. While protonation of bis(2-aminoethyl)amine by 3,5-dihydroxybenzoic acid was to be expected, it is of interest that only the terminal NH_2 groups undergo protonation: the central NH fragment is neither protonated nor a participant in the hydrogen-bonding scheme. This is consistent with the observed stoichiometry, whereas a 1:3 adduct would have been expected if all three N atoms had acted as proton acceptors.

Less predictable was the behaviour of this same amine with 4,4′-sulfonyldiphenol: again, the amine component in (1) is doubly protonated, at the terminal N atoms only, but the pattern of deprotonation of the bis-phenol is entirely different from that observed in the 1:2 adduct with piperazine (Coupar *et al.*, 1996). In this piperazine adduct, the amine is doubly protonated and the two bis-phenol molecules are each singly deprotonated to produce the salt $[C_4H_{12}N_2]^{2+}$.$2(HOC_6H_4SO_2C_6H_4O)^-$. By contrast, in the 1:3 compound (1) one-third of the bis-phenol molecules are doubly deprotonated, while the remainder are neutral: no singly deprotonated ions are present in the crystal structure. The lack of any proton transfer in (2) is consistent with the expected lower acidity of the hydroxyl groups in 1,1,1-tris(4-hydroxyphenyl)ethane compared with those in 4,4′-sulfonyldiphenol.

The adduct formed between tris(2-aminoethyl)amine and 4,4′-biphenol would be expected, on the basis of NH_2/OH complementarity to crystallize with 2:3 stoichiometry, without the incorporation of solvent. As noted previously (Ferguson *et al.*, 1998), this concept is in fact a rather poor predictor of phenol:amine stoichiometry in the majority of systems: it appears to be applicable only when the phenol and the amine are both rigid and of effectively similar shape, so that the apparent complementarity in these examples may, in fact, be adventitious in structures which are actually dominated by other factors.

Overall, however, the complete proton transfers from phenol to amine observed here in (1) and (4) would be unexpected in solution: its observation in the crystalline state is testimony to the influence of the multiple hydrogen bonds, and in particular to the enhanced strength of those hydrogen bonds formed between charged donors and acceptors (Gilli *et al.*, 1994; Bertolasi *et al.*, 1998).

3.2.6. Solvation. In (4) the solvent methanol molecules play an integral role in the overall hydrogen-bonding scheme, as do the methanol molecules in 1,2-diaminoethane–4,4′-biphenol–methanol (1/2/1) (Ferguson *et al.*, 1998). On the other hand, it

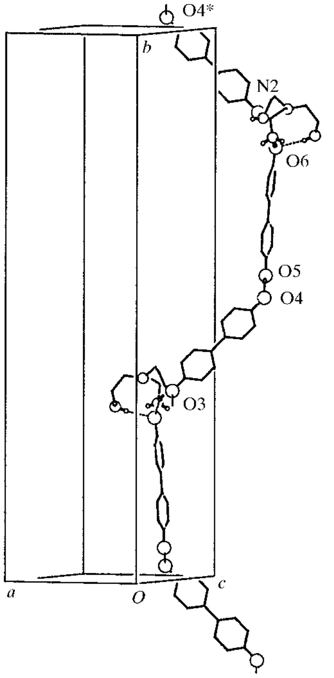

Figure 17
View of part of the crystal structure of (4), showing the $C_3^3(24)$ spiral chain around the screw axis at $(0, y, 1)$. H atoms bonded to C are omitted for the sake of clarity: atoms marked with a star (*) are at symmetry position $(-x, \frac{1}{2}+y, 2-z)$.

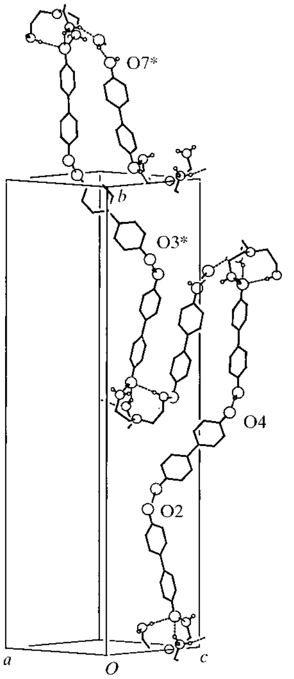

Figure 18
View of part of the crystal structure of (4), showing the $C_7^7(50)$ spiral chain around the screw axis at $(0, y, \frac{1}{2})$. H atoms bonded to C are omitted for the sake of clarity: atoms marked with a star (*) are at symmetry position $(-x, \frac{1}{2}+y, 1-z)$.

is possible to envisage the supramolecular architecture of (2) built exclusively from amine and bis-phenol components, without any structural role for the methanol. Taking this rather passive role of the methanol to its extreme, examples of hydrogen-bonded phenol/amine adducts are known in which methanol molecules are present, but play no part whatsoever in the supramolecular architecture. For example, the 1:2 adduct formed between C-methylcalix[4]resorcinarene and 4,4′-trimethylenebipyridine contains methanol molecules which are not hydrogen bonded to any other component of the structure (Ferguson *et al.*, 1998)

The occurrence of such passive solvation by molecules which are potential hydrogen-bond donors and/or acceptors, but which are not, in the event, all hydrogen bonded to the calixarene is elegantly illustrated by the DMSO and pyridine solvates of the C_{2h} isomer of *C*-(4-hydroxyphenyl)-calix[4]resorcinarene (Shivanyuk *et al.*, 1997). This calixarene can be crystallized with 18 molecules of DMSO or with 14 molecules of pyridine per calixarene unit, respectively: while in each solvate some of the solvent molecules are linked to the calixarene by means of O—H⋯O or O—H⋯N hydrogen bonds, many other solvent molecules are not attached in this manner, and in the DMSO solvate the calixarene units are completely separated from each other by solvent molecules, providing a completely solvated calixarene in the crystalline state. The supramolecular architecture thus represents a solid 'quasi-solution' (Shivanyuk *et al.*, 1997).

3.3. Hydrogen-bond dimensions

It has recently been noted that the criteria for acceptance of non-covalent contacts involving hydrogen as genuine hydrogen bonds seem to be undergoing continual relaxation (Cotton *et al.*, 1997). It therefore seems desirable to specify the acceptance criteria adopted here for the hydrogen bonds listed in Table 2. With the exception of a single outlying value of 3.061 (4) Å for an O⋯O distance in (2), the maximum $D\cdots A$ values in the two-centre hydrogen bonds of O—H⋯O, N—H⋯O and O—H⋯N types are 2.765 (6), 3.153 (4) and 2.840 (9) Å, all typical of their types. The D—H⋯A angles in the two-centre hydrogen bonds are all in the range 140–176°, with a mean value of 163°, very close to the most frequent value of 160° for such two-centre bonds (Jeffrey & Saenger, 1991). For one of the three-centre bonds in (1), the sum of the inter-bond angles at the hydrogen is close to 360°, as is very frequently found for such systems (Jeffrey & Saenger, 1991). Beyond these specifications it is necessary only to note that, as expected, the O⋯O distances in the ionic O—H⋯O$^-$ hydrogen bonds of (1) (O14 as acceptor) and (4) (O1 and O2 as acceptors) are significantly shorter than the neutral O—H⋯O hydrogen bonds listed in Table 2, and that the $D\cdots A$ distances in the planar three-centre system in (1) are rather long, again as expected.

3.4. Molecular conformations and dimensions

3.4.1. The amine components. In (1)–(3) the heavy-atom skeletons of the amine components, which are doubly protonated in (1) and (3), but neutral in (2), adopt entirely different conformations, as judged by the dihedral angles along the chain (Table 3 and Figs. 1, 7, 8 and 11). The neutral amine in (2) adopts an extended-chain conformation in which all the skeletal torsional angles are within 10° of 180° (Fig. 8). Neither of the protonated amines in (1) and (3) adopt this simple conformation: in (3), the N—C—C—N torsion angles are close to ±60°, and the overall conformation is close to C_s symmetry, with the C2–C6 portion of the skeleton almost planar and N1 and N7 both on the same side of this plane (Fig. 11); in (1), on the other hand, the N1–N4 and N4–N7 portions of the cation are quite different so that there is no semblance of symmetry in this unit. In (4) the skeletal conformation of both the independent cations is very close to C_3 symmetry, again as judged by the dihedral angles (Table 3 and Fig. 15).

Since all changes of conformation require only rotation about single C—C or C—N bonds, where the rotational barriers are expected to be small, to shift between conformers which themselves are rather similar in energy, it is likely that the conformations actually observed are dominated by the intermolecular forces, in particular by the hydrogen bonds involving the —NH$_2$ and —NH$_3$$^+$ groups in these amine units.

3.4.2. The phenolic components. In (1) the phenolate dianion $[O_2S(C_6H_4O)_2]^{2-}$ lies across a twofold rotation axis and the neutral bis-phenol $[O_2S(C_6H_4OH)_2]$, although lying in a general position, has a conformation which is close to C_2 molecular symmetry: as usual, the conformation of these units is dominated by the electrostatic interactions between highly polarized sulfone S═O bonds, polarized $S^{\delta+}$═$O^{\delta-}$ and the

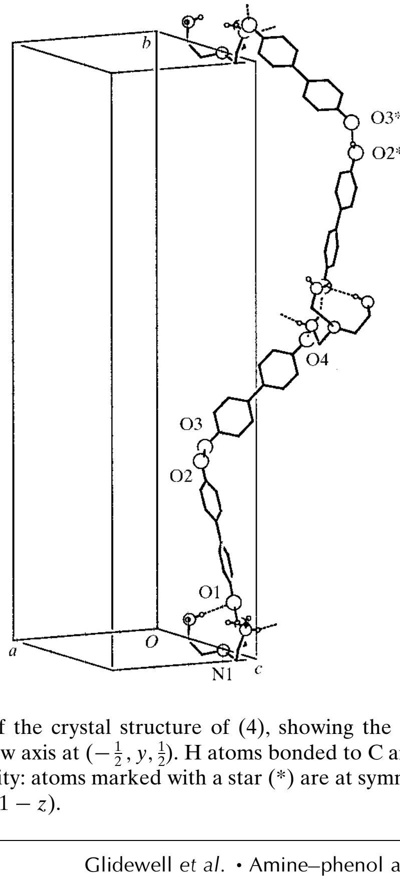

Figure 19
View of part of the crystal structure of (4), showing the $C_3^3(20)$ spiral around the screw axis at $(-\frac{1}{2}, y, \frac{1}{2})$. H atoms bonded to C are omitted for the sake of clarity: atoms marked with a star (*) are at symmetry position $(-1-x, \frac{1}{2}+y, 1-z)$.

adjacent C—H bonds of the aromatic rings which are polarized $C^{\delta-}—H^{\delta+}$(Ferguson *et al.*, 1999). Both units of the trisphenol $CH_3C(C_6H_4OH)_3$ in (2) lie in general positions, but one of them, that containing C71, has a conformation close to C_3 molecular symmetry (Table 3). In (4) the six independent biphenol units are all close to planarity, with a maximum dihedral angle between the rings of only 16.7 (1)°. In a completely planar neutral molecule of 4,4′-biphenol, two conformations, of C_{2h} and C_{2v} symmetry, are possible, differing in the arrangement of the OH groups: one of the neutral biphenol units, that containing O9 and O10, has a C_2 conformation close to C_{2h}; the other four are all close to C_{2v} symmetry (Fig. 15).

The phenolate $C—O^-$ bonds are in general shorter than the corresponding C—OH bonds, as expected, but it is not possible to distinguish unambiguously between $C—NH_2$ and $C—NH_3^+$ bond lengths. Other bond lengths and angles are typical of their types.

4. Conclusions

Two methods, based on the identification of lower-dimensional substructures or on the identification of an appropriate supermolecule, have been used here for the descriptive analysis of complex three-dimensional hydrogen-bonded systems constructed from multiple molecular building blocks. The substructure method proves to be ideal in (1)–(3), while the supermolecule approach is effective both in (1) (where, however, the substructure method was preferred) and in (4), where the substructure approach was inappropriate. In general, for systems of this type both approaches are worthy of investigation. However, it is necessary to enter the caveat that in certain systems, for example diamondoid structures containing two types of building block which occupy alternating positions within the three-dimensional network, neither approach will be capable of providing a coherent analysis.

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